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**WO 00/76929 A1**

(54) Title: BRIQUETTES, THEIR USE IN MINERAL FIBRE PRODUCTION AND THEIR PRODUCTION

(57) Abstract: Man-made vitreous fibres having a composition which contains at least 14 % Al<sub>2</sub>O<sub>3</sub> are produced by melting a mineral charge which includes briquettes and fiberising the melt. In the process the briquettes comprise particulate alumina-containing material having size at least 90 wt. % below 700 µm, Al<sub>2</sub>O<sub>3</sub> content of at least 50 wt. % and at least 20 %, preferably at least 25 %, porosity provided by pores of diameter below 1 µm, measured by mercury porosimetry. Briquettes and processes for producing them are also disclosed.

**BRIQUETTES, THEIR USE IN MINERAL FIBRE PRODUCTION AND THEIR PRODUCTION**

This invention relates to processes of making high alumina content man-made vitreous fibres (MMVF) from a mineral charge which includes briquettes, and to briquettes 5 for this purpose, as well as processes for producing the briquettes.

MMVF may be made by forming a mineral melt by melting a mineral charge in a furnace and fiberising the melt, usually by a centrifugal fiberising process.

10 In some of the furnaces which are used, there is a large pool of melt and the mineral charge is melted into this pool. Examples are tank and electric furnaces. In such furnaces, the physical form (i.e., lump or powder) of the mineral charge is less important since the melting is 15 conducted into a large volume of previously melted material.

However, there is another type of furnace which is used for forming the melt for MMVF production, especially 20 of fibres of the types that are referred to as rock (including stone or slag) fibres. This is a shaft furnace in which the furnace contains a self-supporting column of solid coarse mineral material and combustion gases permeate through this column so as to heat it and cause melting. The melt drains to the bottom of the column, where a pool 25 of melt is usually formed, and the melt is removed from the base of the furnace. Since the column has to be both self-supporting and permeable it is necessary that the mineral material should be relatively coarse and should have considerable strength, despite the high temperatures in the 30 column (which may exceed 1000°C).

The mineral material can be formed of coarsely crushed rock and slag provided this will withstand the pressures and temperatures in the self-supporting column in the shaft furnace. It is known to convert the finer particulate 35 materials such as sands into bonded briquettes for addition to the furnace. These should have sufficient strength and temperature resistance to withstand the conditions in the

self-supporting column in the shaft furnace in order that they melt prior to collapsing.

It is necessary for the total charge in the furnace (i.e., crushed mineral alone or crushed mineral plus 5 briquettes) to provide the composition which is desired for the MMVF fibres which are to be made.

There is a particular interest in the manufacture of MMVF insulation containing more than 14%, and often 18% to 10 30%, alumina, for instance as described in WO96/14274 and WO96/14454. These mention the general concept of use of waste materials as part of the starting material. These include high alumina (20 to 30%) slags such as ladle slag, filter dust and high alumina waste from the production of refractory materials. WO96/14274 describes the production 15 of specified physiologically soluble fibres in various ways, including methods using various furnaces such as electric furnaces and cupola furnaces. The use of aluminium-containing waste materials in general is indeed now known, and in electric furnaces and other furnaces 20 discussed above in which the charged mineral materials are melted directly into a pool of melt the waste material can generally be charged directly into the melt pool in any form, usually as received.

WO97/30002 specifically describes the use of bauxite. 25 In practice bauxite (calcined and/or uncalcined) is the material which has been most widely proposed and used for the manufacture of such fibres.

Unfortunately bauxite is a relatively expensive raw material and the use of bauxite incurs difficulties 30 (additional to its cost) in a shaft furnace containing a self-supporting stack of mineral material.

In a shaft furnace bauxite must be charged in a form which can form part of the self-supporting stack. Thus it can be charged as coarse rock.

35 In shaft furnaces the residence time of material in the small melt pool at the base of the furnace is short, and the raw materials must be incorporated sufficiently

rapidly in this pool of melt if a melt is to be obtained which is suitable for provision of final product having good properties.

Bauxite requires a high temperature for melting, in particular if provided in the form of coarse rock, due to its slow rate of melting. Bauxite can also be provided as part of the briquette component, which requires major energy expenditure to crush and grind the bauxite into a suitable form. However, even when ground into fine particles and incorporated into briquettes, bauxite gives melting problems due to its high melting point. In fact, a proportion of the bauxite does not melt at all but is instead dissolved in the melting zone and in the pool of melt at the base of the furnace. To maximise melting and dissolving of the bauxite in the time available requires provision of fuel, in particular solid fossil fuel such as coke. This increases costs and improves melting. However, if even a small proportion of the bauxite is not melted or dissolved completely, it accumulates in the bottom of the furnace. The accumulated bauxite reduces the volume of the melt pool and the residence time in that pool is thus reduced further. Consequently the accumulated unmelted bauxite must be removed from the furnace from time to time.

Briquettes are particularly useful for forming part, often most, of the charge in a shaft furnace. They may also be used as part of the charge in an electric furnace. Briquettes are a useful vehicle for adding to the furnace components of the charge which have small size. These include waste from MMVF production processes (MMVF waste). MMVF waste is a useful and economical component for inclusion in briquettes but tends to have a rather high moisture content. This may for instance be around 10 to 15%, but may be up to 80%. This moisture content can arise due to contact of the fibres with water as they are being removed from the base of the spinning chamber or other stage of the production process from which they come. This moisture content, if high, can cause difficulties in

formation of briquettes. In particular the strength of the briquettes may be affected.

WO98/30512 describes a binder system for the production of briquettes. It acknowledges that calcined bauxite is known for use as a binder in the production of briquettes. This publication described an alternative binder produced by sintering a mixture of crude bauxite and marl and then grinding the sintered product. The binder is apparently intended as a replacement for Portland cement and appears to have a particle size distribution in which substantially all particles have size below 50 µm. Although production of mineral fibre products is mentioned generally, there is no indication of specific fibre types for which the briquettes containing the defined binder should be used.

It would be desirable to be able to provide materials suitable for the production of high alumina fibres which can be incorporated into briquettes which form a strong self-supporting stack in a shaft furnace but also melt sufficiently rapidly and uniformly that they release their constituents evenly into the melt, in particular in comparison with briquettes containing ground bauxite. It would at the same time be desirable to provide materials which are suitable as components of briquettes which contain MMVF waste or other moisture-containing material without the attendant problems which can arise.

Surprisingly, we have found that it is possible to alleviate both the problem of melting and the problem of moisture in the briquettes by selection of raw materials having a defined combination of properties. In particular we find that materials having defined size, alumina content and surface area are especially beneficial.

According to the invention we provide a process of producing man-made vitreous fibres having a composition which contains at least 14% aluminium (measured as weight Al<sub>2</sub>O<sub>3</sub> based on oxides) by providing in a furnace a mineral charge which includes briquettes, melting the charge to

provide a melt, removing melt from the furnace and fiberising the melt, characterised in that the briquettes comprise particulate alumina-containing material which has a size at least 90% by weight below 700 microns, alumina 5 content at least 50% by weight of the material and porosity measured by mercury porosimetry (as discussed below) such that the percentage of pores of size below 1  $\mu\text{m}$  is at least 20%, preferably at least 25%.

We find that the combination of small size and high 10 porosity defined means firstly that the particulate material has improved melting and dissolution properties in the furnace, especially in a shaft furnace such as a cupola furnace, in comparison with crushed bauxite. This is achieved despite the high content of alumina, which is very 15 similar to that of bauxite. We also find that the combination of high surface area and small size influences the interaction of the particulate material with moisture-containing materials in briquettes.

The particulate alumina-containing material has a 20 defined small size of at least 90% by weight below 700 microns. Preferably at least 90 wt. % are below 600 microns, more preferably below 500 microns. In particular, it is preferred that at least 90 wt. % are below 300 microns, more preferably below 250 microns. It is also 25 preferred that at least 50 wt. % of the particles have a size at least 30 microns, and preferably at least 60 wt. % have a size at least 40 microns. Preferably the average particle size is from 30 to 100 microns, preferably 40 to 80 microns. Particle size can be measured by known laser 30 scattering techniques (eg using the Malvern technique).

Porosity of the particulate material is determined using mercury porosimetry. Porosity is measured for pores from diameter 0.0100 to 1000.000  $\mu\text{m}$ . Porosity can be measured using an Autopore II 9220 apparatus, available 35 from the company Micromeritics. An appropriate penetrometer should be chosen according to the usage

instructions and we find that part numbers 920-61714-00 and 920-61716-00 are often appropriate.

Using this method it is possible to establish the percentage of total porosity which is given by pores of size less than 1  $\mu\text{m}$ . This is at least 20%, preferably at least 25 or 30% and particularly preferably at least 35%.

The percentage of porosity provided by pores of size less than 1  $\mu\text{m}$  is established as follows. The cumulative intrusion is plotted (for the pore size range discussed above) against pore diameter. The total cumulative intrusion at pore diameter 0.01  $\mu\text{m}$  can be designated as x. The cumulative intrusion at diameter 1  $\mu\text{m}$  can be designated as y. The percentage porosity given by pores below size 1  $\mu\text{m}$  can therefore be calculated from the following relationship:

$$\text{percentage porosity below } 1 \mu\text{m} = 100 - [(y/x) \times 100].$$

This mercury porosimetry measurement method also gives a value of total pore area and this value is preferably at least 4  $\text{m}^2/\text{g}$ , more preferably at least 6, in particular at least 8 or 10  $\text{m}^2/\text{g}$  and in particular at least 12  $\text{m}^2/\text{g}$ .

This mercury porosimetry method also gives a value of porosity and this value is preferably at least 40%, more preferably at least 45 or 55%.

Details of suitable analysis conditions are set out in Example 2 below.

Preferably the material also has multi-point surface area measured by BET analysis of at least 2  $\text{m}^2/\text{g}$ , preferably at least 10  $\text{m}^2/\text{g}$ .

In this case, the surface area of the particulate material is the multi-point surface area value given by BET analysis. This value is preferably at least 2  $\text{m}^2/\text{g}$ , more preferably at least 10  $\text{m}^2/\text{g}$ , most preferably at least 20  $\text{m}^2/\text{g}$ . It may in particular be at least 30  $\text{m}^2/\text{g}$  and particularly preferably at least 50  $\text{m}^2/\text{g}$ .

BET analysis also gives a value of single point surface area and preferably this property also has the preferred values given above.

BET analysis is a well known technique and may be carried out using any suitable apparatus, in particular the Gemini 2360 apparatus available from the company Micromeritics. Details of suitable analysis conditions are 5 set out in Example 3 below.

It is believed that the selection of materials having the defined porosity and preferred surface area values improves the melting and dissolution properties of the particulate material, especially in the environment of a 10 shaft furnace.

We believe that the porosity and surface area are also influential in controlling the behaviour of the particulate material in contact with moisture during briquette formation.

15 Preferably also the particulate material is substantially inert to moisture. By "substantially inert" we mean that the material undergoes substantially no chemical reaction with moisture under the conditions to which it is subjected during the briquetting process.  
20 Temperature of briquetting may range from room temperature (eg about 25°C) up to about 60°C and the material is inert under these conditions. For instance cement briquettes are produced at around room temperature and molasses briquettes (form stones) may be formed at temperatures up to 60°C.  
25 Briquetting pressure may be around 20 kN/line centimetre in the case of molasses briquettes and the material should be inert under these conditions. Cement briquettes are often made by vibrating the particulate material in a mould without substantial pressure and the particulate material  
30 should not react chemically with moisture under these conditions. In general, the material is inert under conventional briquetting conditions.

We believe that particulate materials which are inert to moisture under the briquetting conditions give 35 advantages over those which are not inert and which undergo substantial reaction with moisture. We find that materials according to the invention absorb or adsorb water easily,

thus alleviating briquetting problems with moisture-containing materials, but since they do not chemically react with the water they release it easily when charged to the furnace. We believe that the water absorbed or adsorbed  
5 into or onto the particulate material may be driven off at a temperature of around 100°C, whereas if the material reacts with water a temperature of from 200 to 400°C would be necessary. With this preferred feature of the invention it is possible to ensure that most or all of the absorbed  
10 water is driven off at the top of a shaft furnace, where the temperature is relatively low. This avoids the necessity to use additional energy further down a shaft furnace to drive off water when this could better be used for melting the charge.

15 Furthermore, the inert raw material can have advantages when the overall moisture content of the raw materials used to form the briquettes is rather low. In some briquetting processes a low level of moisture (eg at least 0.5% or at least 1% by weight of the mixture used for  
20 moulding the briquettes, up to 5% or 3%) is advantageous for reaction with binder. Where the general level of moisture is low the material of the invention can adsorb or absorb moisture but give it up during the briquetting process (if necessary for reaction with the binder) since  
25 it has not chemically reacted with the moisture.

Suitable preferred particulate alumina-containing materials can be defined in terms of their hygroscopicity. In particular, they can be defined by means of the percentage increase in weight (based on weight before  
30 testing) of the particulate material when it is exposed to relative humidity of 90% at 20°C for 24 hours. Preferably the weight increase is at least 2 wt. %, more preferably at least 4 wt. %, in particular around 5 wt. % or greater.

In particular, preferred materials have this  
35 hygroscopicity without being provided with extremely fine particle size. Thus, the material preferably has both the

preferred minimum particle sizes discussed above and the preferred hygroscopicity properties.

Suitable materials which can be used as the particulate alumina-containing material include activated 5 bauxite. This can be made in known manner, eg by roasting gibbsite at around 400 to 800°C.

Particularly preferred materials are filter dusts from the calcination of bauxite and other processes involving heating and/or calcination of high alumina materials, in 10 particular in the production of refractory materials.

Various filter dusts are known from a wide variety of processes, and various wastes are known from the production of high alumina refractories, but the majority do not have the combination of chemical analysis and physical 15 properties discussed above. However, filter dusts can be found with these properties. The filter dust as received may have the defined particle size range but if not it can be subjected to treatment such as sieving in order to provide this particle size range.

20 It is particularly beneficial in the invention to be able to use materials of this type because they are generally waste products and are normally sent to landfill after collection. Thus use of these materials provides both an economical means for obtaining the properties essential 25 in the invention and a use for a material which would otherwise be dumped.

The filter dust can be obtained as a by-product of the process of calcination of bauxite. This is carried out for instance during the production of materials for 30 refractories, use in MMVF products and abrasives.

Dust from the calcination of bauxite in the production of pure alumina may be used. In this process bauxite containing  $\text{Al(OH)}_3$  is calcined in a furnace. Suitable furnaces include rotary kilns, stationary calciners, round 35 kilns, shaft kilns and reverberatory furnaces, although rotary furnaces are most common. Flue gas from this process contains fine solids which may be separated from

the gas, for instance by filtration or electrostatic precipitation. The solids collected are the filter dust.

Before calcination the coarse Al(OH)<sub>3</sub> is washed. It is then sent to the furnace, optionally after being 5 dewatered and dried. Usually it is the flue gas from the furnace (e.g. rotary kiln) which provides the filter dust.

In a stationary calciner the washed Al(OH)<sub>3</sub> is dewatered and dried, often in a flash dryer and often with hot gas. Solids and gas are separated so that solids are 10 passed to further processing. However, some filter dust may be recovered from the gas at this stage either by filtration or electrostatic precipitation. This filter dust may be used as the particulate material in the invention. The solids then are passed to further heating 15 stages to ensure calcination. From these stages the flue gas is also recovered and filter dust from this, obtained by filtration or electrostatic precipitation, may also be used in the invention.

Preferably however the particulate alumina-containing 20 material is filter dust obtained from processes of refractory production. In this process bauxite is calcined in a furnace such as a rotary kiln or a shaft furnace at temperatures of around 1,100 to 1,650°C. This sinters the bauxite and reduces its porosity. The flue gas from this 25 process is usually cleaned, for instance by a precipitator (eg electrostatic) or by filtration and the solid product (eg precipitate or filtrate) obtained can be used in the invention. Preferably the dust is obtained from precipitators used in such a process for cleaning the flue 30 gas from a rotary kiln.

Filter dusts of these types may have (as received) particle size distribution as follows, in which case they can be used in the invention without modification:

30 to 60% below 60 microns

35 30 to 70% from 63 to 212 microns

5 to 20% from 125 to 250 microns

0.5 to 8% from 250 to 500 microns

0 to 3% from 0.5 to 1mm

0 to 1% above 1mm

Descriptions of processes in which bauxite is calcined and from which filter dusts suitable in the invention can be obtained can be found in Ullmann's Electronic Encyclopedia of Industrial Chemistry, 6th Edition, 1998, Chapter 3.1.7 "Calcination" (in the production of alumina) and Industrial Minerals 03/97, pp 21 ff.

The particulate material has content of alumina of from 50 to 99%, preferably 60 to 95%, more preferably 75 to 90%, eg 80 to 88%, by weight of the material. The preferred filter dusts discussed above are particularly advantageous because they have chemical composition very similar to that of bauxite. They tend to have higher ignition loss, around 2 to 8%, in comparison with below 1% for calcined bauxite.

Other components may include  $\text{SiO}_2$  (up to 10 or 5%),  $\text{Fe}_2\text{O}_3$  (up to 5 or 3%),  $\text{TiO}_2$  (up to 4 or 3%),  $\text{CaO}$  (up to 0.5 or 0.1%),  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$  (up to 1 or 0.5% total).

The particulate material before inclusion in the briquettes preferably has water content below 10% by weight based on dry weight of the material. The preferred filter dusts generally have water content below 1%.

The fibres produced in the invention have high aluminium content (measured by weight of  $\text{Al}_2\text{O}_3$ ), namely at least 14%, preferably at least 15%, more preferably at least 16% and in particular at least 18%. Generally the amount of aluminium is not more than 35%, preferably not more than 30%, more preferably not more than 26 or 23%.

In general the fibres and the melt from which they are formed have an analysis (measured as % by weight of oxides) of other elements within the various ranges defined by the following normal and preferred lower and upper limits :

$\text{SiO}_2$ : at least 30, 32, 35 or 37; not more than 51, 48, 45 or 43

$\text{CaO}$ : at least 2, 8 or 10; not more than 30, 25 or 20

$\text{MgO}$ : at least 2 or 5; not more than 25, 20 or 15

FeO (including Fe<sub>2</sub>O<sub>3</sub>): at least 2 or 5; not more than 15, 12 or 10

FeO+MgO: at least 10, 12 or 15; not more than 30, 25 or 20

5 Na<sub>2</sub>O+K<sub>2</sub>O: zero or at least 1; not more than 10

CaO+Na<sub>2</sub>O+K<sub>2</sub>O: at least 10 or 15; not more than 30 or 25

TiO<sub>2</sub>: zero or at least 1; not more than 6, 4 or 2

TiO<sub>2</sub>+FeO: at least 4 or 6; not more than 18 or 12

10 B<sub>2</sub>O<sub>3</sub>: zero or at least 1; not more than 5 or 3

P<sub>2</sub>O<sub>5</sub>: zero or at least 1; not more than 8 or 5

Others: zero or at least 1; not more than 8 or 5

The invention is of particular value in the production of fibres which can be shown to be soluble in physiological saline. Suitable high aluminium, biologically soluble, fibres which can advantageously be made in the present invention are described in WO96/14454 and WO96/14274. Others are described in WO97/29057, DE-U-2970027 and WO97/30002. Reference should be made to each of these.

20 The fibres preferably have an adequate solubility in lung fluids as shown in vivo tests or in vitro tests, typically conducted in physiological saline buffered to about pH 4.5. Suitable solubilities are described in WO96/14454. Usually the rate of dissolution is at least 10 or 20nm per day in that saline.

The fibres preferably have sintering temperature above 800°C, more preferably above 1000°C.

30 The melt preferably has a viscosity at fibre forming temperature of 5 to 100 poise, preferably 10 to 70 poise, at 1400°C.

In the invention the furnace is preferably a shaft furnace (as discussed above) in which a self-supporting stack of mineral material is heated and melt drains to the base of the stack. Usually it forms a pool from which it 35 is run off to the fibre-forming process. In some cases the melt can be run from the base of the stack into another chamber where it collects as pool and from which it is run

off to the fibre-forming process. The preferred type of shaft furnace is a cupola.

The invention is preferably applied in a shaft furnace but it can provide benefits in other furnaces such as tank 5 and electric furnaces in which a large pool of melt is provided into which the mineral charge is melted.

It is essential in the invention that the charge includes briquettes. The briquettes are made in known manner by molding a mix of the desired particulate 10 materials (including the high alumina material) and a binder into the desired briquette shape and curing the binder.

The binder may be a hydraulic binder, that is one which is activated by water, for instance cement such as 15 Portland cement. Other hydraulic binders can be used as partial or complete replacement for the cement and examples include lime, blast furnace slag powder (JP-A-51075711) and certain other slags and even cement kiln dust and ground MMVF shot (US 4662941 and US 4724295).

20 Alternative binders include clay. The briquettes may also be formed with an organic binder such as molasses, for instance as described in WO95/34514; such briquettes are described herein as form stones.

The invention has particular benefits when the 25 briquettes include materials which are provided having moisture content, in particular moisture content above about 5%. These include power plant bottom ash, water quenched metallurgical slags, paper sludge and sewage sludge and MMVF waste. As discussed above the latter tends 30 have a significant moisture content as a result of exposure to water during transfer from the base of the spinning chamber or other position in the production process from which it comes. MMVF waste obtained from the screw conveyor below the spinner tends to have moisture content 35 around 5%. MMVF waste retrieved from the cleaning of the spinning chamber tends to have moisture content from 20 to 80%. Although these mineral wool wastes may be subjected

to mechanical pressing prior to use, normally they are not otherwise dried. Therefore preferably in the invention the briquettes comprise at least 25 wt.% MMVF waste, preferably at least 45 wt.%. However, they generally do not comprise 5 more than 80 wt.% and preferably comprise less than 65 wt.%.

Other moisture-containing materials may be present in amounts of up to 30 wt.% and include those mentioned above.

10 The moisture-containing materials such as MMVF waste tend to cause difficulty during the briquetting process in particular when the binder is molasses, although there can be problems with clay briquettes and to a lesser extent cement briquettes.

15 Preferably at least 10%, more preferably at least 15 or 20%, of the aluminium in the melt, measured by weight  $\text{Al}_2\text{O}_3$ , is provided by the defined particulate aluminium-containing material. Preferably at least 25% and even 30% or more of the aluminium may be provided by this material.

20 The briquettes comprise the particulate aluminium-containing material. Generally all of the aluminium-containing particulate material included in the charge is included as a component of the briquettes.

25 Generally at least 20 to 25%, preferably at least 30% of the charge (by weight) is provided by briquettes. In some processes higher amounts, e.g. 45 to 55%, are preferred and amounts above 75% or even above 80% are sometimes preferred. The invention is especially beneficial in processes where a significant (e.g. above 25%) proportion of the charge is in the form of briquettes.

30 The briquettes generally contain (by weight) at least 5% of the defined aluminium-containing mineral, preferably at least 10 or 15%. They may contain more than 20% but generally do not contain more than 45 or 50% of the defined aluminium-containing material.

35 The other materials in the briquettes and in the rest of the charge may be any suitable virgin or waste materials. Other suitable wastes that can be used in the

invention include slags from the metallurgical industry, especially steelmaking slags such as converter slags or EAF slags, and slags from the ferro-alloy industry such as ferro-chromium, ferro-manganese or ferro-silica slags; 5 slags and residues from the primary production of aluminium such as spent aluminium pot lining or red mud; dried or wet sludge from the paper industry; sewage sludge; molasses; bleaching clay; residues from the incineration of household and industrial wastes, especially slags or 10 filter ashes from the incineration of municipal solid wastes; glass waste (or slags) from the vitrification of other waste products; glass cullet; waste products from the mining industry, especially minestone from the excavation of coal; residues from the incineration of 15 fossil fuel, especially from the combustion of coal at power plants; spent abrasive sand; spent moulding sand from iron and steel casing; waste sieving sand; glass reinforced plastic; and fines and breakage waste from the ceramic and brick industry. Toxic virgin rock can also be 20 used as waste.

The MMV fibres may be made from the fibre-forming mineral melt in conventional manner. Generally they are made by a centrifugal fibre-forming process. For instance the fibres may be formed by a spinning cup process in which 25 they are thrown outwardly through perforations in a spinning cup, or melt may be thrown off a rotating disc and fibre formation may be promoted by blasting jets of gas through the melt. Preferably a cascade spinner is used and fibre formation is conducted by pouring the melt onto the 30 first rotor in a cascade spinner. Preferably the melt is poured onto the first of a set of two, three or four rotors, each of which rotates about a substantially horizontal axis, whereby melt on the first rotor is primarily thrown onto the second (lower) rotor although 35 some may be thrown off the first rotor as fibres, and melt on the second rotor is thrown off as fibres although some

may be thrown towards the third (lower) rotor, and so forth.

The MMV fibres may be used for any of the purposes for which MMVF products are known. These include fire insulation and protection, thermal insulation, noise reduction and regulation, construction, horticultural media, and reinforcement of other products such as plastics and as a filler. The materials may be in the form of bonded batts (which may be flat or curved) or the materials 5 may be comminuted into a granulate. Bonded batts include 10 materials such as slabs and pipe sections.

The preferred materials may also be defined independently (but less preferably) in terms of their surface area. Therefore in a second aspect the invention 15 provides a process of producing man-made vitreous fibres having a composition which contains at least 14% aluminium (measured as weight  $\text{Al}_2\text{O}_3$  based on oxides) by providing in a furnace a mineral charge which includes briquettes, melting the charge to provide a melt, removing melt from 20 the furnace and fiberising the melt, characterised in that the briquettes comprise particulate alumina-containing material having size at least 90% below 700  $\mu\text{m}$ , alumina content of at least 50 wt.% and multi-point surface area measured by BET analysis of at least 2  $\text{m}^2/\text{g}$ , preferably at 25 least 10  $\text{m}^2/\text{g}$ .

Preferably this material and process have all of the preferred properties discussed above in connection with the first aspect of the invention, as well as the defined BET multi-point surface area.

30 The invention also provides briquettes (and processes for their production) containing the particulate alumina-containing materials discussed above, preferably at least 5 wt. % of these materials.

In these aspects of the invention, any of the 35 preferred features discussed above, where applicable, may be applied also.

Example 1

Each of the examples below describes briquette components of a charge for a cupola furnace which can be incorporated into a melt which can be fiberised, for instance using a cascade spinner.

5    Formstone Briquettes

(A)    8% molasses  
          4% burnt lime  
          25% particulate alumina-containing material (PACM)  
          5% olivine sand  
10      58% MMVF waste.  
  
(B)    8% molasses  
          4% burnt lime  
          22% particulate alumina-containing material (PACM)  
          4% olivine sand  
15      6% paper mill sludge  
          56% MMVF waste.

Clay Briquettes

20      50% Clay  
          12% PACM  
          6% olivine sand  
          4% slag  
          20% MMVF waste.

Cement Briquettes

25      12% cement  
          15% PACM  
          8% incineration slag  
          17% diabase split  
          48% MMVF waste

Example 2

30      This example sets out mercury porosimetry data for samples of a material suitable for use in the invention and comparative results for milled bauxite. The data was obtained using an Autopore II 9220 apparatus available from the company Micromeritics, using software version V3.03.

35      Milled Bauxite

Penetrometer Number:        14/0078  
Advancing Angle:            130.0 deg

Penetrometer Constant: 10.79  $\mu\text{L}/\text{pF}$   
Receding Contact Angle: 130.0 deg  
Penetrometer Weight: 63.6179 g  
Mercury Surface Tension: 485.0 dyn/cm

5 Stem Volume: 0.4120 mL  
Mercury Density: 13.5335 g/mL  
Maximum Head Pressure: 0.0323 MPa  
Sample Weight: 0.9197 g  
Penetrometer Volume: 3.1679 mL

10 Sample+PEN+Hg Weight: 100.6238 g  
Low Pressure:  
Evacuation Pressure: 50  $\mu\text{mHg}$   
Evacuation Time: 15 min  
Mercury Filling Pressure: 0.0202 MPa

15 Equilibration Time: 15 sec  
High Pressure:  
Equilibration Time: 15 sec  
Blank Correction by File Blank /g  
Blank Correction File ID: b1 14/0078

20 Intrusion Data Summary  
(From Diameter 0.0100 to 1000.0000  $\mu\text{m}$ )  
Total Intrusion Volume = 0.2056 mL/g  
Total Pore Area = 1.024 sq-m/g  
Median Pore Diameter (Volume) = 4.2408  $\mu\text{m}$

25 Median Pore Diamter (Area) = 0.0573  $\mu\text{m}$   
Average Pore Diameter (4V/A) = 0.8032  $\mu\text{m}$   
Bulk Density = 1.8342 g/mL  
Apparent (Skeletal) Density = 2.9449 g/mL  
Porosity = 37.71%

30 Stem Volume Used = 46%  
Invention (Filter dust obtained from electrostatic precipitators used for cleaning the gas from rotary kiln used for calcination of bauxite in refractory production)  
Penetrometer Number: 16/0931

35 Advancing Contact Angle: 130.0 deg  
Penetrometer Constant: 21.63  $\mu\text{L}/\text{pF}$   
Receding Contact Angle: 130.0 deg

Penetrometer Weight: 61.0300 g  
Mercury Surface Tension: 485.0 dyn/cm  
Stem Volume: 1.1980 mL  
Mercury Density: 13.5335 g/mL  
5 Maximum Head Pressure: 0.0323 MPa  
Sample Weight: 1.0288 g  
Penetrometer Volume: 4.0825 mL  
Sample+PEN+Hg Weight: 105.4566 g  
Low Pressure:  
10 Evacuation Pressure: 50  $\mu\text{mHg}$   
Evacuation Time: 15 min  
Mercury Filling Pressure: 0.0202 MPa  
Equilibration Time: 15 sec  
High Pressure:  
15 Equilibration Time: 15 sec  
Blank Correction by File Blank /10  
Blank Correction File ID: b1 16/0931  
Intrusion Data Summary  
(From Diameter 0.0100 to 1000.0000  $\mu\text{m}$ )  
20 Total Intrusion Volume = 0.4795 mL/g  
Total Pore Area = 12.950 sq-m/g  
Median Pore Diameter (Volume) = 4.3839  $\mu\text{m}$   
Median Pore Diamter (Area) = 0.0323  $\mu\text{m}$   
Average Pore Diameter (4V/A) = 0.1491  $\mu\text{m}$   
25 Bulk Density = 1.1614 g/mL  
Apparent (Skeletal) Density = 2.6209 g/mL  
Porosity = 55.60%  
Stem Volume Used = 41%  
Figures 1 and 2 demonstrate the relationship between  
30 cumulative intrusion and pore diameter. Figure 1 (for milled bauxite) shows that total cumulative intrusion is around 0.21 mL/g. Approximately 85% (0.18/0.21) is provided by pores of size above 1  $\mu\text{m}$ , shown by the value of cumulative intrusion of 0.18 mL/g at 1  $\mu\text{m}$  pore diameter.  
35 Therefore 100-85, namely approximately 15%, is provided by pores of size below 1  $\mu\text{m}$ . Figure 2 shows that approximately 36% porosity is provided by pores of diameter

below 1  $\mu\text{m}$  in the case of the filter dust of the invention (0.30 ml/g cumulative intrusion at 1  $\mu\text{m}$  out of total 0.47 ml/g).

When the particle size was measured for both samples 5 using a Malvern laser scattering instrument, the milled bauxite had size 97% below 600  $\mu\text{m}$  and the filter dust had size 99% below 600  $\mu\text{m}$ .

Example 3

The data below was measured by BET analysis by methods 10 appropriate for determining the BET values preferred in the invention. The data below sets out the properties, measured by BET, of samples of a material suitable for use in the invention and comparative results for milled bauxite. The data was obtained using a Gemini No. 2360 15 apparatus, available from the company Micromeritics. Software used was version 2.01.

Milled Bauxite

Sample Weight: 2.8033 g

Saturation Pressure: 789.57 mmHg

20 Measured Free Space: 2.550 cc STP

Evacuation Time: 2.0 min

Analysis Mode: Equilibration

Equilibration Time: 5 sec

25 BET Multipoint Surface Area Report

Surface Area: 0.9120 sq. m/g

Slope: 4.751581

Y-Intercept: 0.021866

30 C: 218.306885

V<sub>m</sub>: 0.209492

Correlation Coefficient: 9.9983e-001

BET Single Point Surface Area: 0.8942 sq. m/g

Total Pore Volume at 0.8006 P/P<sub>0</sub>: 0.0009 cc/g.

35 Invention (Filter dust obtained from electrostatic precipitators used for cleaning the gas from rotary kiln used for calcination of bauxite in refractory production)

21

Sample Weight: 1.7727 g  
Saturation Pressure: 789.57 mmHg  
Measured Free Space: 3.859 cc STP  
Evacuation Time: 2.0 min  
5 Analysis Mode: Equilibration  
Equilibration Time: 5 sec

## BET Multipoint Surface Area Report

10 Surface Area: 56.7870 sq. m/g  
Slope: 0.075801  
Y-Intercept: 0.000857  
C: 89.435165  
Vm: 13.044900  
15 Correlation Coefficient: 9.9999e-001  
BET Single Point Surface Area: 55.1197 sq. m/g  
Total Pore Volume at 0.7997 P/Po: 0.0514 cc/g.

Example 4

The following are charges which can be charged to a  
20 furnace such as a cupola furnace, melted and fiberised.

(i) 51% diabase  
12% blast furnace slag  
7% converter slag  
30% formstone briquettes (A) as in Example 1.

25 (ii) 8% diabase  
7% converter slag  
75% clay briquettes as in Example 1  
10% cement briquettes comprising:

30 9% cement  
20% pit melt  
41% bauxite (finely ground)  
30% olivine sand

35 (iii) 40% diabase  
10% limestone  
50% cement briquettes as in Example 1.

Claims

1. A process of producing man-made vitreous fibres having a composition which contains at least 14% aluminium measured as weight Al<sub>2</sub>O<sub>3</sub> based on oxides, comprising
  - 5 providing in a furnace a charge of mineral material which includes briquettes,
    - melting the charge to provide a melt,
    - removing melt from the furnace and fiberising the melt,
  - 10 characterised in that the briquettes comprise particulate alumina-containing material having size at least 90 wt. % below 700 microns, a content of Al<sub>2</sub>O<sub>3</sub> of at least 50 wt.% and at least 20%, preferably at least 25%, porosity provided by pores of diameter below 1 µm, measured
  - 15 by mercury porosimetry as described herein.
2. A process according to claim 1 in which the particulate material has multi-point surface area measured by BET analysis of at least 2 m<sup>2</sup>/g, preferably at least 10 m<sup>2</sup>/g.
- 20 3. A process according to claim 1 or claim 2 in which the particulate material has a total pore area at least 4 m<sup>2</sup>/g, preferably at least 6 m<sup>2</sup>/g, measured by mercury porosimetry as described herein.
- 25 4. A process according to any preceding claim in which the particulate material has a porosity of at least 45%, measured by mercury porosimetry as described herein.
5. A process according to any preceding claim in which the particulate material undergoes substantially no reaction with moisture under the conditions of formation of
- 30 the briquettes.
6. A process according to any preceding claim in which the particulate material has a size at least 90 wt. % below 500 microns, preferably at least 90 wt. % below 250 microns.
- 35 7. A process according to any preceding claim in which the particulate material increases in weight by at least 2%

based on the pre-treated weight of the particulate material when exposed to 90% relative humidity for 24 hours at 20°C.

8. A process according to claim 7 in which the particulate material increases in weight by at least 4%.

5 9. A process according to any preceding claim in which the briquettes comprise a material which before briquetting has a moisture content of at least 5 wt.%.

10. A process according to any preceding claim in which the briquettes comprise mineral wool waste material, preferably in an amount of at least 25% by weight of the briquette.

15 11. A process according to any preceding claim in which the briquettes additionally comprise a binder, preferably a binder selected from the group consisting of hydraulic binders, clay and organic binders.

12. A process according to any preceding claim in which the briquettes additionally comprise a binder which is clay or molasses.

20 13. A process according to any preceding claim in which the briquettes contain at least 15%, preferably at least 20%, of the particulate material.

25 14. A process according to any preceding claim in which at least 10%, preferably at least 20%, by weight measured as  $\text{Al}_2\text{O}_3$ , of the aluminium in the charge is provided by the particulate material in the briquettes.

30 15. A process according to any preceding claim in which the particulate material is filter dust obtained by filtration or precipitation of flue gas from a furnace used for calcination of bauxite, preferably during production of refractory materials.

16. A process according to any of claims 1 to 14 in which the particulate material is activated bauxite.

35 17. A process according to any preceding claim in which the particulate material has a size at least 50 wt. % above 50 microns.

18. A process according to any proceeding claim in which the particulate material has a size at least 60 wt.% above 40  $\mu\text{m}$ .
19. A process according to any preceding claim in which 5 the furnace is a shaft furnace in which the mineral charge is a self-supporting stack, preferably a cupola furnace.
20. A briquette suitable for the production of man-made vitreous fibres containing a particulate alumina-containing material containing at least 50 wt.%  $\text{Al}_2\text{O}_3$ , having size at 10 least 90 wt.% below 700  $\mu\text{m}$  and having porosity measured by mercury porosimetry as described herein such that at least 20%, preferably at least 25%, of the porosity is provided by pores having size below 1  $\mu\text{m}$ .
21. A briquette according to claim 20 containing at least 15 5%, by weight of the briquette, of the defined particulate material, preferably at least 15%, more preferably at least 20%.
22. A process for the production of a briquette suitable 20 for the production of man-made vitreous fibres comprising providing a particulate alumina-containing material containing at least 50 wt.%  $\text{Al}_2\text{O}_3$ , having size at least 90% by weight below 700  $\mu\text{m}$  and porosity measured by mercury porosimetry as described herein such that at least 20%, preferably at least 25%, of the porosity is provided by 25 pores of size below 1  $\mu\text{m}$ , providing other particulate materials, and moulding and bonding the particulate materials to form a briquette.
23. A process according to claim 22 comprising providing binder selected from hydraulic binders, clay and molasses.

1/1

Fig.1.

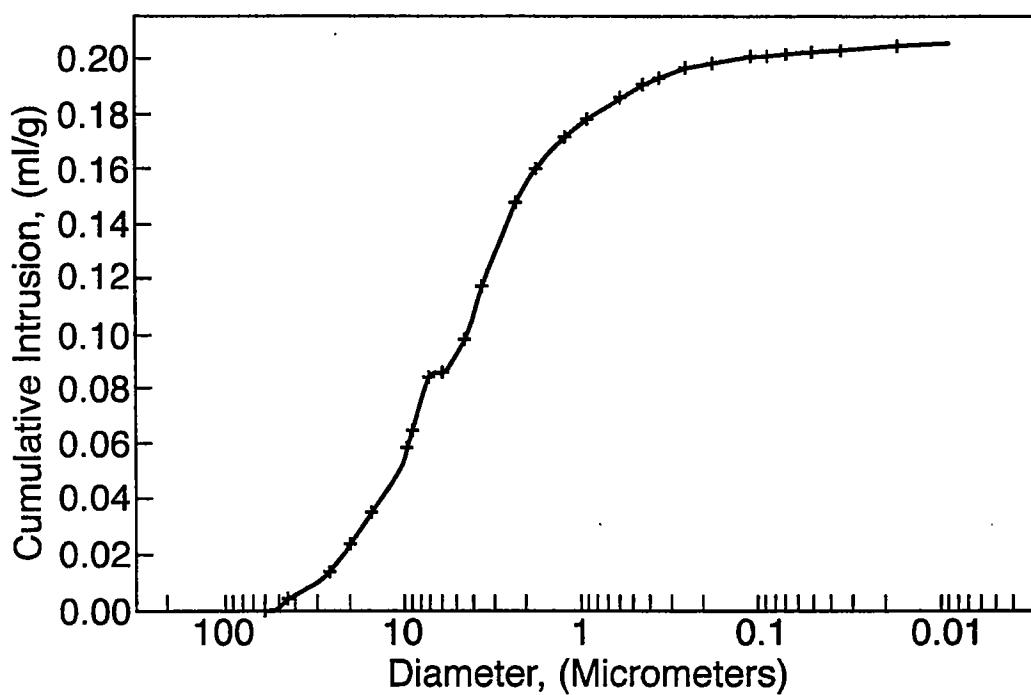
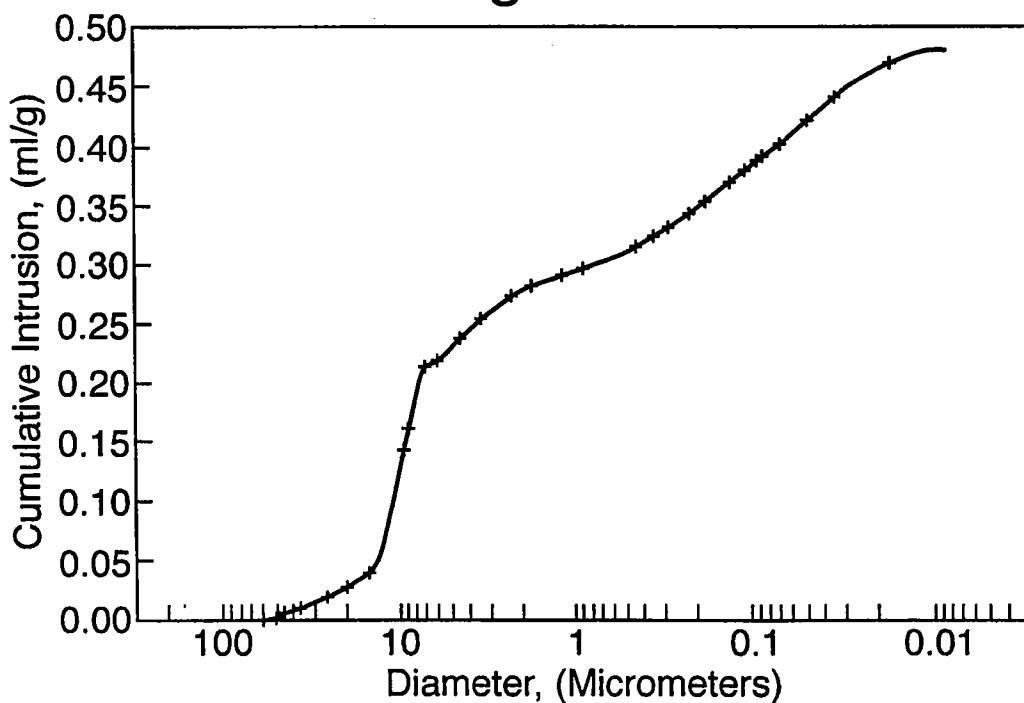


Fig.2.



# INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 00/05281

**A. CLASSIFICATION OF SUBJECT MATTER**  
 IPC 7 C03C13/00 C03C1/02 C03C1/00

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)  
 IPC 7 C03C C03B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

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Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

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Date of the actual completion of the international search

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## INTERNATIONAL SEARCH REPORT

Inte onal Application No

PCT/EP 00/05281

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